

1 Language

- Atoms: Smallest unit of an element
- Elements: Substances made of only one atom type
- Molecules: Two or more atoms joined together
- Compounds: Molecules with different types of atoms
- Reactions: Describe "chemical changes"

1.1 Mixtures

Contain 2 or more pure substances

- homogeneous mixture: uniform mixture
- heterogeneous mixture: non uniform mixture

1.2 Dalton's atomic theory

- constant composition
- conservation of mass
- multiple proportions

1.3 Atomic structure

see mass and charge of electrons, protons and neutrons on web

- Atoms have equal number of protons and neutrons
- all masses are tiny, but neutron and proton much heavier than electron

Definitions

- Atomic number: Number of protons
- Isotopes: Same element with different number of neutrons
- Mass number: number of protons and neutrons
- Atomic symbols: $\frac{\text{Mass number}}{\text{Atomic number}} \text{Element}$ or ${}^{12}_6C$
- Atomic mass scale: ${}^{12}C$ defined as 12u
- Atomic weight: average atomic mass of element and its isotopes in u

1.4 Atomic table

Atomic number, Symbol and weight are shown with every known element

- Group 1: Alkali metals
- Group 2: Alkaline earth metals
- in between: Lanthanides and Actinides
- Group 3-12: Transition metals
- Group 16: Chalcogens
- Group 17: Halogens
- Group 18: Noble gases

1.5 Molecules and compounds

Only noble gases as isolates atoms Representation:

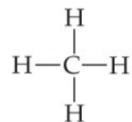


Figure 1: structural formula

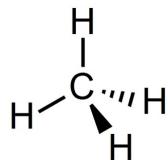


Figure 2: perspective drawing

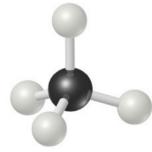


Figure 3: Ball-and-stick model



Figure 4: space-filling model

polyatomic ions: Ions made from a group of atoms
Ionic compounds:

- cations, generally metal & anions, generally non-metal
- oppositely charged ions attract each other
- compound in total charge neutral

1.6 reactions

- chemical Reactions: changes of substances (chemical properties)
 - Atoms neither created / destroyed during reaction
 - Energy may be required to start, may be absorbed / released
- chemical equations: reactants \rightarrow products
 - Stoichiometry: balance chemical equations
 - Formula weight: sum of atomic weights of atoms in formula
- the Mole: $6.022 \cdot 10^{23} = N_A$ = Avogadro's number, atomic weight of any element in grams contains N_A atoms \rightarrow molar mass
- limiting reactant: bottleneck in reaction because more of that one reactant would be needed for the reaction to work

2 types of reactions

- combination reactions: A + B \rightarrow C
- decomposition reactions: C \rightarrow A + B

3 gases

3.1 Variables

- Volume V
- Amount n (moles)
- Temperature T
- Pressure P

3.2 Pressure

$P = \frac{F}{A} = \rho \cdot g \cdot h = \left[\frac{N}{m^2} \right] = [Pa]$ Pressure created by randomly moving molecules that his surfaces in Manometer: $P_{gas} = P_{atm} + \rho \cdot g \cdot h$

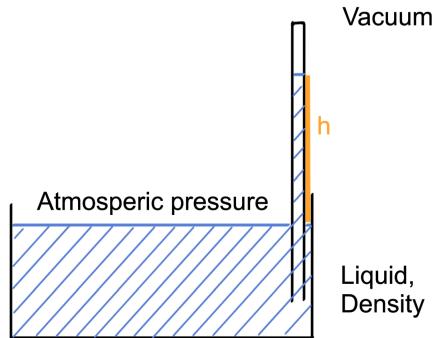


Figure 5: Barometer

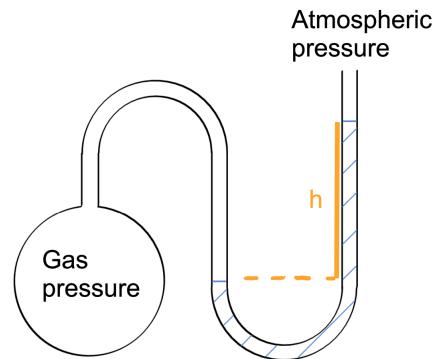


Figure 6: Manometer

3.3 (ideal) gas laws

molecules dont interact, volume that molecules occupy much smaller than total volume

- IGL $P \cdot V = n \cdot R \cdot T$, Gas constant $R = 8.314 \frac{m^3 \cdot Pa}{mol \cdot K}$
- Boyle's law / first gas law: $P \cdot V = const$
- Charle's law / second gas law: $\frac{V}{T} = const$
- Avogadro's law / third gas law: $\frac{V}{n} = const$
- STP ($T = 0^\circ C = 273.15K$, $P = 1atm = 101.325kPa \rightarrow$ Volume per mole of gas $V = 22.41L$)

- rearranging IGL: $\rho = \frac{P}{R \cdot T} \cdot MW$, molecular weight
- rearranging IGL: $MW = \frac{\rho \cdot R \cdot T}{P}$
- Dalton's law of partial pressures: $P_{tot} = P_1 + P_2 + \dots + P_i$
- mixtures: $X_i = \frac{n_i}{n_{tot}} \rightarrow P_i = \frac{n_i}{n_{tot}} \cdot P_{tot} = X_i \cdot P_{tot}$

3.4 gas molecule movement

Velocity Distribution: Kurve wie bei Wahrscheinlichkeitsverteilung der Augenzahl auf Würfel $V_{rms} = \sqrt{\frac{3 \cdot R \cdot T}{M_W}}$ warmer gases or lighter molecules \rightarrow faster movement

Diffusion: Spread of substance through space much slower than its velocity as it collides on its way

Mean Free Path: Average distance between collisions (1atm \rightarrow 60 nm)

nonidealities in gases: generally: Low temperature \rightarrow molecules start interacting with each other Low pressure $\rightarrow \frac{PV}{RT}$ lower than ideal gas High pressure $\rightarrow \frac{PV}{RT}$ higher than ideal gas & volume occupied by molecules no longer negligible (not needed in exam) Van der Waals equation describes nonidealities in gases: $(P + \frac{n^2 a}{V^2}) \cdot (V - nb) = n \cdot R \cdot T$

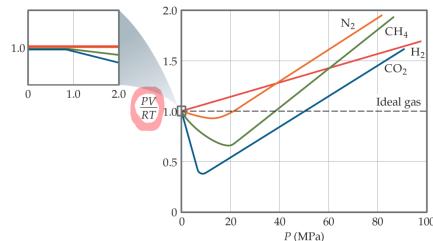


Figure 7: Nonidealities in gases

4 (Aqueous) solutions and types of rxns

4.1 Reactions in Aqueous solutions

- Solution = solvent + solutes
- Aqueous solution: H_2O as solvent
- Electrolytes: Substance that dissolves in H_2O by forming ions
- Nonelectrolytes: Substance that dissolves in H_2O without forming ions

4.2 Precipitation Reactions

- Precipitate: solid formed by rxn in solution
- General Form: $AX + BY \rightarrow AY + BX$
- Complete Ionic Equation: $A^+ + X^- + B^+ + Y^- \rightarrow AY + B^+ + X^-$
- Net ionic Equation: $A^+ + Y^- \rightarrow AY$ (no spectator ions)
- Precipitation rxns are also Exchange or Metathesis Rxns

4.3 Acid-Base reactions

- Acid: Substance ionizes in H_2O to form/donate hydrogen cations H^+
- Base: Substance that reacts with/accept hydrogen cations H^+
- Strength depends on amount of H^+/OH^- produced
- reactivity also depends on anion
- Neutralization rxn: H^+ and OH^- form H_2O

4.4 Redox-Reactions

- Oxidation: When an atom, ion or molecule loses electrons \rightarrow Atom, ion, molecule becomes positively charged, Ox number increases
- Reduction: When an atom, ion or molecule accepts electrons, Ox number decreases
- Redox reaction involves an oxidation and a reduction
- Oxidation numbers: monoatomic ions \rightarrow oxidation number is same as charge, neutral molecules or polyatomic ions: hypothetical charge - elemental form: Ox number = 0 - monoatomic ions: Ox number = ionic charge - nonmetals in compounds: negative Ox number - O \rightarrow -2 (peroxide ion \rightarrow -1) - H \rightarrow +1 (nonmetals), \rightarrow -1 (metal) - F \rightarrow -1 sum of Ox number in compounds = net charge
- Activity Series: List of metals in decreasing ease of oxidation - any metal can be oxidized by metal cations below it - Any metal above hydrogen on list can react with acid to form H_2

5 Thermodynamics I

5.1 1st law of thermodynamics

Energy can be converted between different types (potential Energy in chemical bonds and kinetic Energy), but neither created nor destroyed

$\Delta E = q + w$, q is heat added to system , w is work done on system Endothermic rxn for $q > 0$, Exothermic for $q < 0$

- Open system: Matter and Energy exchanged with surroundings
- Closed system: Energy exchanged with surroundings
- Neither Matter nor Energy exchanged

$\Delta E = E_{\text{final}} - E_{\text{initial}}$, if $\Delta E > 0$ system has gained Energy

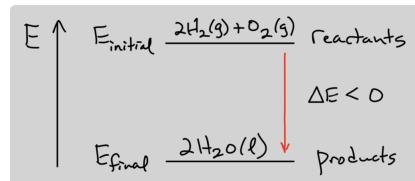


Figure 8: Energy Diagram

5.2 State Functions

Value only depends on current state, not on path taken to get there, ex. Energy E, Enthalphy H while q and w are not state functions

5.3 Enthalpy

aka Heat of rxn

- $H = E + PV$ (Pressure-Volume work)
- $\Delta H = \text{heat at constant } P: \Delta H = \Delta E + P\Delta V = q_P + w - w = q_P$
- $\Delta H - \Delta E = P\Delta V$: for small $\Delta V \rightarrow \Delta H \approx \Delta E$
- also: ΔH_{fus} : heat of fusion (solid \rightarrow liquid)
- also: ΔH_{vap} : heat of vaporization (liquid \rightarrow vapor)

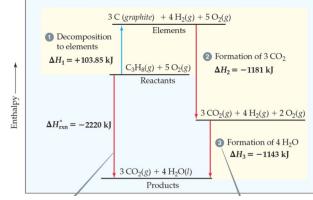


Figure 9: Enthalpy Diagram

5.4 Calorimetry

Total Energy of a mass, Heat Capacity with $\Delta T = 1K$

- molar heat capacity $q = n \cdot c_m \cdot \Delta T$
- specific heat capacity $q = m \cdot c_s \cdot \Delta T$

5.5 Hess's Law

$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3 \dots$$

5.6 Enthalpies of Formation

ΔH_f^o : Elements at STP (Standard T and P) \rightarrow Compound 1mol at STP
 $\Delta H_{rxn} = \Delta H_f^o$

6 Thermodynamics II

6.1 Definitions

Spontaneous process

- If process is spontaneous in one direction \rightarrow nonspontaneous in the other
- Experimental conditions matter (ex. T for ice melting)
- nonspontaneous \neq impossible

Reversible and irreversible

- Reversible: Process can be reversed with no change to surroundings
- Process that reverses direction after infinitesimal change to property of system (idealised T, ideal gas)
- Irreversible: Surroundings are changed when process is reversed

Statements

- All spontaneous processes are irreversible
- return system to initial state requires work
- Energy spreads out

6.2 Entropy S

- Measure of tendency for E to spread
- state function
- $\Delta S = S_{final} - S_{initial}$
- $\Delta S = \frac{q_{rev}}{T}$

6.3 2nd Law of thermodynamics

- Reversible Process: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{Surr} = 0$
- Irreversible Process: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{Surr} > 0$
- Entropy of universe increases for any spontaneous process

6.4 Boltzmann's Equation

$$S = k_B \cdot \ln(W)$$

W = number of microstates consistent with specific macroscopic state k_B = Boltzmann constant $= 1,38 \cdot 10^{-23} J/kg$

Entropy measures number of microstates consistent with state -> measure of spread in energy or amount of randomness or disorder in system (Messung der Unordnung) Entropy of system increases with number of microstates $\Delta S = k_B \cdot \ln(W_{final}) - k_B \cdot \ln(W_{initial}) = k_B \cdot \ln(\frac{W_{final}}{W_{initial}})$

$$R = k_B \cdot N_A$$

In general W and S increase with

- Increase in system's V
- Increase in system's T
- Increase in number of molecules
- Increase in complexity of molecules
- Melting of solids
- Vaporizing of liquids

6.5 3rd Law of thermodynamics

if $\Delta T < 0$ -> less Energy in system

$T = 0K$ -> $S = 0$ means: only one microstate at 0K

6.6 Gibbs Free Energy G

Goal of System: Lower H and increase S

$G := H - T \cdot S$ (Herleitung Lecture 5)

If $\Delta G < 0$ spontaneous If $\Delta G > 0$ nonspontaneous If $\Delta G < 0$ irreversible If $\Delta G = 0$ reversible

6.7 Importance of Temperature T

rxns are spontaneous for $\Delta G < 0$

Example	ΔH	ΔS	$-T\Delta S$	ΔG	Spontaneous at:
$2O_3 \rightarrow 3O_2$	-	+	-	-	all T
$3O_2 \rightarrow 2O_3$	+	-	+	+	no T
$H_2O(l) \rightarrow H_2O(s)$	-	-	+	+ or -	low T
$H_2O(s) \rightarrow H_2O(l)$	+	+	-	+ or -	high T

7 Electronic Structure

electrons determine reactivity electrons form bonds -> molecules

7.1 Light

- wave with wavelength λ which colour depends of
- Wave has frequency $\nu = \frac{c}{\lambda}$
- Light waves carry energy $E = h \cdot \nu = \frac{h \cdot c}{\lambda}$

-> photons -> duality of light

7.2 Bohr Model

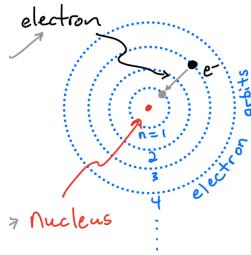


Figure 10: Bohr's atom model

- Electron can occupy only certain orbits
- Electron then has specific "allowed" energies, E_n

- Electron can move between allowed orbits
- requires absorption or emission of photon with $E_{ph} = h\nu$

7.3 Orbital Energies

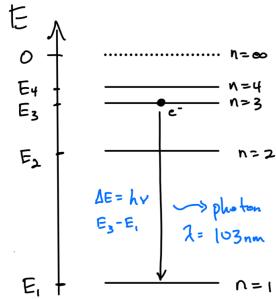


Figure 11: Orbital energies

$$E_n = -\frac{h \cdot c \cdot R_H}{n^2}, \Delta E_n = -h \cdot c \cdot R_H \cdot \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

Energy levels specified with n
Limitations:

- Cannot explain stable orbits
- Can only explain H

7.4 Quantum mechanics

- Resolves limitations of Bohr model
- uncertainty Principle: $\Delta x \cdot \Delta p \geq \frac{\hbar}{4\pi}$, x is position, p is momentum
- Electron motion described by its λ
- Due to uncertainty principle, we only know probabilities
- Bohr orbits become atomic orbitals
- Orbital description:
 - principal quantum number n : size of orbital
 - Angular Quantum Number l : depends on n , shape of orbital
 - Magnetic Quantum Number m_l : range of m_l depends on l , Orientation of orbital space
 - Spin magnetic quantum number m_s : $+\frac{1}{2}$ or $-\frac{1}{2}$, electrons act like they spin but they do not

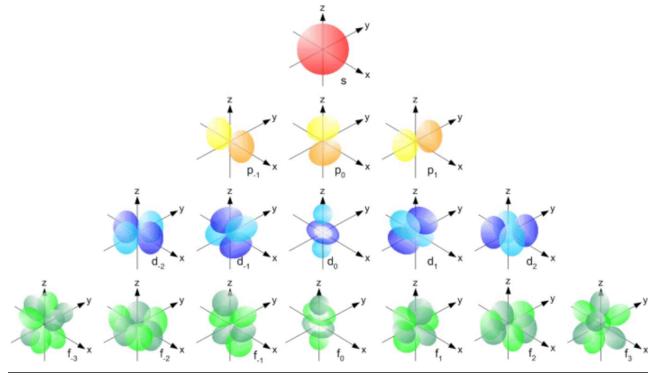


Figure 12: Atomic orbitals

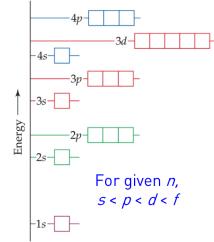


Figure 13: Energy diagram for subshells in quantum mechanics

TABLE 6.3 Electron Configurations of Several Lighter Elements						
Element	Total Electrons	1s	2s	2p	3s	Electron Configuration
Li	3	[1]	[1]			1s ² 2s ¹
Be	4	[1]	[1]			1s ² 2s ²
B	5	[1]	[1]	[1]		1s ² 2s ² 2p ¹
C	6	[1]	[1]	[1] [1]		1s ² 2s ² 2p ²
N	7	[1]	[1]	[1] [1] [1]		1s ² 2s ² 2p ³
Ne	10	[1]	[1]	[1] [1] [1]		1s ² 2s ² 2p ⁶
Na	11	[1]	[1]	[1] [1] [1]	[1]	1s ² 2s ² 2p ⁶ 3s ¹

Figure 14: Electron configurations of lighter elements

TABLE 6.2 Relationship among Values of n , l , and m_l through $n = 4$						
Possible n Values of l	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell		
1	0	1s	0	1	1	
2	0	2s	0	1		
	1	2p	1, 0, -1	3	4	
3	0	3s	0	1		
	1	3p	1, 0, -1	3		
	2	3d	2, 1, 0, -1, -2	5	9	
4	0	4s	0	1		
	1	4p	1, 0, -1	3		
	2	4d	2, 1, 0, -1, -2	5		
	3	4f	3, 2, 1, 0, -1, -2, -3	7	16	

Figure 15: How to label atomic orbitals

Energy of different subshells within same shell now different due to electrons repelling each other

- Pauli exclusion principle: No two electrons in the same atom can have identical values for all 4 quantum numbers.
- Hund's rule: If we have a choice to place electrons in a subshell, make spin parallel first before pairing up electrons.

7.5 Order of subshell

For lighter elements follow the line of the periodic table to see which atom fills which shells Notation for valence electrons: ex Se -> [Ar]4s²3d¹4p⁴ Exceptions exist

7.6 Screening

Electrons getting in each others way

- Valence Electrons (VE's) repelled by core electrons -> $Z_{eff} < Z$, Core electrons "screen" nucleus
- Effect stronger for subshells further from nucleus
- Z_{eff} increases across row in PT

Z is nuclear charge

7.7 Atomic Size

- Bonding atomic radius = $\frac{d}{2}$ for bond length d (see tables)
- Trends: Atomic radii tend to increase down and decrease across period (going right) ($\Delta Z_{eff} > 0$)
- Ionic radii: cations smaller, anions bigger

7.8 Ionization Energy

Energy needed to rip an electron off Trends: I increases left to right, decreases down group

7.9 Electron affinity

Energy change when we add extra electron to atom Trends: Halogens EA ≈ 0 ; noble gases EA ≈ 0

8 Chemical Bonding

involve valence electrons

- Ionic (electrostatic attraction)
- Covalent (sharing valence electrons)
- Metallic (valence electrons shared with entire solid)

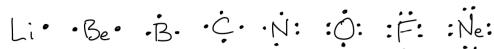


Figure 16: lewis symbols

Octet rule: Atoms want 8 valence electrons Exceptions:

- Odd number of electrons
- Less than octet v.e. (formal charges more important than octet rule)
- more than octet of v.e. (beyond period 3 in PT)

8.1 Ionic bonding

higher melting point, brittle Metal atoms as v.e. donor, Non-metal as v.e. acceptor strong bondings lattice energy: energy required to separate the bonding calculate lattice energy: $NaCl^- \rightarrow Na(s) + Cl(g)^- \rightarrow Na(g) + Cl(g)^- \rightarrow$ Ionisation energy – > electron affinity == lattice energy electronegativity ≈ 2

8.2 Covalent bonding

lower melting / boiling point two atoms share their v.e. Possibilities:

- Two atoms share 1 pair: single bond (less strong)
- Two atoms share 2 pairs: double bond (generally shorter bond)
- Two atoms share 3 pairs: triple bond (even shorter bond, stronger)

bonding pair drawn as a line, unshared non-bonding v.e. kept as dots ex: Cl_2 erfüllt noble gas configuration Strength of covalent bonds:

- listed: average Enthalpy change / energy required to break bond
- $\Delta H_{rxn} = \sum$ Enthalpies for bonds broken – \sum Enthalpies for bonds formed

8.3 polarity and Electronegativity

- Bond polarity
 - equal: nonpolar covalent bonding (both atoms pull on the electrons with the same strength, ex Cl-Cl)
 - unequal: polar covalent bonding (ex H-F)

Electronegativity: ability of atom to attract e^- estimation of polarity the higher Electronegativity, the higher ionization energy

calculation: see values in table $\Delta EN = EN_1 - EN_2$ ρ^+ partial positive charge ρ^- partial negative charge EN increases to right an top of periodic table

8.4 Dipole moment

$\vec{\mu}$ Separations of charge quantified by vector ppinging from negative to positive charge $|\vec{\mu}| = Q \cdot r \pm Q$ = charges separated by distance r Unit: Debye $D = 3.34 \cdot 10^{-30} C \cdot m$

8.5 Ionic vs. Covalent

fliessender Übergang As oxidation number of metal increases -; bonding more covalent

8.6 Lewis Structures

1. Sum v.e. of all atoms
2. Write symbols and connect with single bonds
3. Complete octets around non-central atoms
4. Place remaining v.e.'s around central atom
5. Try multiple bonds if central atom does not have octet

If more than one lewis structure is possible: formal charge on specific atom = atom's v.e.'s - $\frac{1}{2}$ (atom's bonding e^-) - (atoms nonbonding e^-) negative formal charges on more electronegative atoms

8.7 Oxidation number vs. Formal Charge vs. Partial Charge

- Oxidation number:
 - Charges atoms would have if bonds completely ionic
 - Shared e's given completely to more electronegative atom
 - Overestimates role of electronegativity

- Formal charge: Charges atoms would have if
 - bonding e's shared equally
 - Ignores electronegativity
- Partial charge:
 - somewhere in between

8.8 Resonance Structures

Two alternative but equivalent Lewis structures ex. Benzene O_3, C_6H_6



Figure 17: Resonance structure of Benzene

8.9 Strengths of covalent Bonds

- Enthalpy change for breaking particular bond
- Positive number: energy required to break bond
- $\Delta H_{rxn} = \sum$ enthalpies broken bonds – \sum enthalpies formed bonds
- more bonds: stronger bond: less distance between atoms

8.10 Molecular shape

- Lewis structures do not show 3D shape
- Shape = connectivity + bond angles
- Size = shape + bond lengths

prediction:

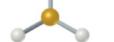
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	 Linear	2	0	 Linear	$\ddot{\text{O}}=\text{C}=\ddot{\text{O}}$
3	 Trigonal planar	3	0	 Trigonal planar	$\ddot{\text{F}}\text{B}\ddot{\text{F}}_2$
		2	1	 Bent	$[\ddot{\text{O}}=\ddot{\text{N}}=\ddot{\text{O}}]^-$
4	 Tetrahedral	4	0	 Tetrahedral	CH_4
		3	1	 Trigonal pyramidal	NH_3
		2	2	 Bent	H_2O
5	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	PCl_5
		4	1	 Seesaw	SF_4
		3	2	 T-shaped	ClF_3
		2	3	 Linear	XeF_2
6	 Octahedral	6	0	 Octahedral	SF_6
		5	1	 Square pyramidal	BrF_3
		4	2	 Square planar	XeF_4

Figure 18: Possible molecular geometries

- linear - trigonal planar - tetrahedral - trigonal bipyramidal - octahedral
 VSPER model: - electrons pairs move as far apart as possible - 5 basic shapes and bond angles - bonds and lone pairs arranged around central atom (com-

parison balloons) - Shape determined by number of electron domains around central atom

lone pairs take up more space predict shape:

1. Draw Lewis structure
2. Count electron domains
3. Determine electron-domain geometry
4. Determine molecular geometry from position of atoms

Hypervalent atoms: period 3 and beyond, can have more than 4 e^- pairs, lone pairs occupy positions with most space

9 Intermolecular Forces

- Intramolecular bonding
- interactions between molecules

9.1 Properties of Phases

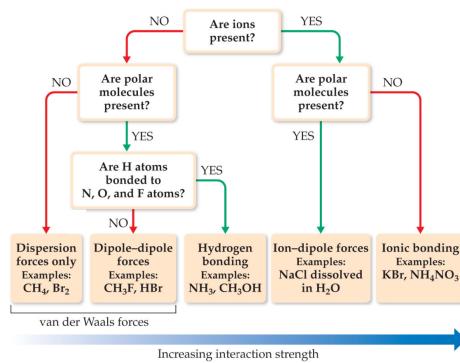
Question	Gas	Liquid	Solid
Is the container filled?	Y	N	N
takes shape of container?	Y	Y	N
Flows?	Y	Y	N
Are molecules Close to each other? Ordered?	N	Y	Y
Are molecules ordered?	N	N	Y
Compressible?	Y	N	N
$E_{interaction} \leftrightarrow E_k$	ii	almost =	ii

- E_{int} depends on distance, d
- $E_{int} < 0$ vs. E_k
- T decreases $\rightarrow E_k$ decreases relative to E_{int}

9.2 Ion-Dipole Interactions

important in solutions Molecule orients its polar δ^+ or δ^- to negative or positive ion - ζ . Polar solvents are good solvents for ions

9.3 Intermolecular interactions



Neutral molecules

1. Dispersion : Induced Dipole - Induced Dipole, attractive at short distances

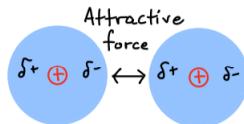


Figure 19: Dispersion force

2. Dipole-Dipole: molecular dipoles interact (Polar molecules have a Molecular dipole moment (vector sum of all bond dipole moments))
3. Hydrogen Bonding (special Dipole-Dipole)

- N, O, F (high EN) create very polar bonds with H
- H is attracted to unbounded e^-
- small H can get close → large E_{int}

1 and 2 together: Van-der-Waals Kräfte: always present and attractive

- increases with molecule size
- affected by molecule shape

Interatomic bonds \angle Ion-Dipole \angle H-Bonding \angle Dipole-Dipole =about Dispersion Atoms repell when pushed into each others electron cloud

9.4 Properties of liquids

- Viscosity higher if E_{int} higher: Resistance of flow
- Surface Tension higher if E_{int} higher: Energy per area of liquid surface At surface, interaction of molecules is missing - \downarrow Molecules try to minimize surface
- Vapor Pressure: pressure of molecules in gas phase
 - molecules with $E > E_{int}$ [E is E_k of specific molecule] enter gas phase
 - low E_{int} : volatile liquid escaping fraction increases with rising T
 - Dynamic equilibrium
- Phase Change
 - changing between Solid, Liquid, Gas: see phase diagram
 - ΔH_{fus} = Heat of fusion
 - ΔH_{vap} = Heat of vaporization
 - ΔH_{sub} = Heat of sublimation
 - $\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$
 - $\Delta H_{vap} > \Delta H_{fus}$

9.5 Phase Diagram

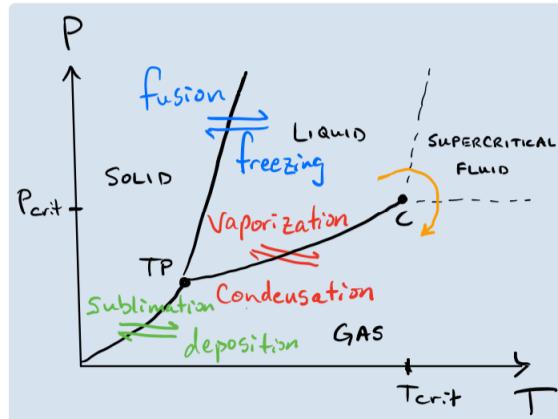


Figure 20: Phase Diagram

- Plots T on x-axis and P on y-axis
- TP: three phases co-exist

- C: Critical point
- critical point: highest T, P where distinct liquid phase exist, beyond: supercritical fluid
- T_{mP} (melting point) typically increases with increasing P
- T_{bP} (boiling point) increases with increasing P

9.6 Clausius-Clapeyron Equation

$$\ln(P_{vap}) = \frac{-\Delta H_{vap}}{R \cdot T} + C \quad C = \text{absolute T}, R = \text{gas constant}, C = \text{constant}$$

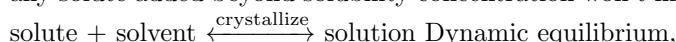
10 Properties of solutions

ΔG_{soln} spontaneous if $\Delta G = \Delta H_{soln} - T\Delta S_{soln} < 0$

- $\Delta H_{soln} > 0$ typically
- $\Delta H_{soln} = \Delta H_{solvent} + \Delta H_{solute} + \Delta H_{mix}$, can be + (Endothermic) or - (Exothermic)
 1. $\Delta H_{solvent}$: (solvent)_n → n· solvent
 2. ΔH_{solute} : (solute)_m → m· solute
 3. ΔH_{mix} : (solvent)_n + (solute)_m → solution
- $\Delta H_{soln} < 0$ typically completely miscible (mixable)
- $\Delta H_{soln} > 0 \rightarrow T\Delta S_{soln}$ must be sufficient negative, more likely at high T

10.1 Solubility

any solute added beyond solubility concentration won't mix: saturated solution



Dynamic equilibrium,
factors:

- intermolecular forces: Substances with similar intermolecular interactions tend to be soluble in each other
- Pressure: $S_g = k \cdot P_g$ gas solubility = Henry's law constant , gas partial pressure
- Temperature
 - Ion solubilities in H_2O increase with T
 - Gas solubilities in H_2O decrease with T

10.2 Expressions for concentration

- X Mole fraction = $\frac{\text{molessolute}}{\text{totalmoles}}$
- M Molarity = $\frac{\text{molessolute}}{\text{literssolution}}$
- m Molality = $\frac{\text{molessolute}}{\text{kgsolvent}}$
- Mass % = $\frac{\text{massolute}}{\text{totalmass}} \cdot 100$
- ppm = $\frac{\text{massolute}}{\text{totalmass}} \cdot 10^6$
- ppb = $\frac{\text{massolute}}{\text{totalmass}} \cdot 10^9$

10.3 Colligative Properties

Colligative: properties of liquid only depend on amount of solute

1. Boiling-Point Elevation: $\Delta T_{bp} = T_{bp}^{\text{soln}} - T_{bp}^{\text{pure}} = i \cdot K_b \cdot m$, m = molality, K_b = molal bp elevation constant, i = van't Hoff factor (1 for non-electrolytes, else number of ions produced for electrolytes ($i = 2$ for NaCl)))
2. Vapor-Pressure Lowering (ideal solution): boiling liquid $\rightarrow P_{vap} = P$, Raoult's law: $P_{vap}^{\text{soln}} = X_{\text{solvent}} \cdot P_{vap}^{\text{pure}}$ for volatile solvent + non-volatile solute
3. Freezing-Point Depression: $\Delta T_{fp} = T_{fp}^{\text{soln}} - T_{fp}^{\text{pure}} = -i \cdot K_f \cdot m$ (used for anti-icing)
4. Osmosis: solutions separated by membrane, that only passes solvent more solvent flows (net flow) to one side until equilibrium osmotic flow: equalizes concentrations osmotic pressure: counteracts osmotic flow (hydrostatic pressure) Osmotic Pressure: $\Pi \cdot V = i \cdot n \cdot R \cdot T \rightarrow \Pi = i \cdot M \cdot R \cdot T$ isotonic $\Pi = \Pi_{ref}$ hypertonic $\Pi > \Pi_{ref}$ hypotonic $\Pi < \Pi_{ref}$

10.4 Ideal solution

- All intermolecular interactions identical
- solu - solv \downarrow solv - solv — solu - solu - \downarrow $P_{vap}^{\text{soln,actual}} > P_{vap}^{\text{ideal}}$
- solu - solv \downarrow solv - solv — solu - solu - \downarrow $P_{vap}^{\text{soln,actual}} < P_{vap}^{\text{ideal}}$

11 Chemical kinetics

- Thermodynamics: tells if "driving force" exists
- chemical kinetics describe speed of rxn (concentration, time, temperature) and info about how rxn occurs (rxn mechanism)

11.1 Reaction Rate

quantification of speed of rxn:

$$\text{Rxn rate} = \frac{\text{change in concentration of reactants or products}}{\text{time interval}} \text{ Unit: } [\frac{M}{s}]$$

$$A \rightarrow A \text{ rxn rate} = \text{rate of appearance of B} = \text{rate of disappearance of A}$$

$$= \frac{\Delta[B]}{\Delta t} = -\frac{\Delta[A]}{\Delta t}$$

$$\text{Average rxn rate: } \frac{\Delta[B]}{\Delta t} = \frac{\Delta[B]_{t_2} - \Delta[B]_{t_1}}{\Delta t_{t_2-t_1}} \text{ instantaneous rxn rate: } \frac{d[B]}{dt}$$

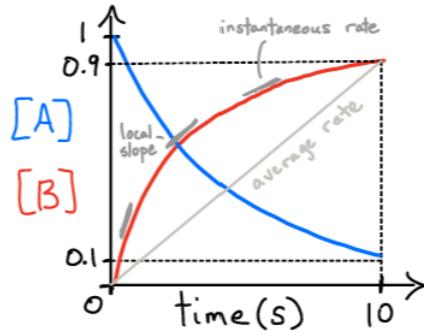


Figure 21: Plotting the reaction rate

If average rate = instantaneous rate: linear plot

- rxn rate does not depend on concentration C
- Bottleneck in reaction (cookie factory analogy)

11.2 Terminology

- rate = instantaneous rate at t
- initial rate = instantaneous at $t = 0$
- general rxn: $\alpha A + \beta B \rightarrow \gamma C + \delta D$
- rate = $-\frac{1}{\alpha} \frac{d[A]}{dt} = -\frac{1}{\beta} \frac{d[B]}{dt} = -\frac{1}{\gamma} \frac{d[C]}{dt} = -\frac{1}{\delta} \frac{d[D]}{dt}$

11.3 rate laws

- general rxn: general rate law Rate = $k [A]^m [B]^n$, $m + n + p\dots$ = reaction order
- k rate constant
- m, n reaction orders (not necessarily equal to $\alpha, \beta\dots$)
- rate law given by experimental measure, Ex: $A + B \rightarrow C$, Rate = $k [A]^m [B]^n$,

Exp	[A] M	[B] M	Initial rate ($\frac{M}{s}$)
1	0.1	0.1	$4 \cdot 10^{-5}$
2	0.1	0.2	$4 \cdot 10^{-5}$
3	0.2	0.1	$16 \cdot 10^{-5}$

-> Rate 2, Rate 3
Rate 1, Rate 1

- Note 1: more reactants -> Rate = $k [A]^m [B]^n [C]^p$, rxn order = $m+n+p$
- Note 2: unit of k = $\frac{M}{s \cdot M^{m+n+p} \dots}$
- Note 3: Fast rxn: $k \geq 10^9$, slow rxn: $k \leq 10$
- using Rate laws: determine how concentration change with time
 - First order reactions: $-\frac{d[A]}{dt} = k[A]$
 $\rightarrow \int_{[A]_0}^{[A]_\tau} \frac{d[A]}{dt} = -k \int_0^\tau dt \rightarrow \ln\left(\frac{[A]_\tau}{[A]_0}\right) = -k\tau$ or $[A]_\tau = [A]_0 \cdot e^{-k\tau}$
 - plotting: slope = k
 - * if plot $[A]_t$ vs t yields line: zero order rxn
 - * if plot $\ln([A]_t)$ vs t yields line: 1st order rxn
 - * if plot $\frac{1}{[A]_t}$ vs t yields line: 2nd order rxn

11.4 Reaction half-life

- First Order: $t_{\frac{1}{2}} = \frac{0.693}{k}$
- Second Order $t_{\frac{1}{2}} = \frac{0}{k[A]_0}$
- Zero Order $t_{\frac{1}{2}} = \frac{[A]_0}{2k}$

12 Rxn mechanisms, Catalysts

- Collision Model: Rate \propto Collisions per second
- higher T \rightarrow molecules collide more often / forcefully
- Small percentage of collisions \rightarrow reaction, depending on:
 - E_{kin} (Activation Energy)
 - orientation

12.1 Activation Energy

E_a = Activation Energy = Energy needed to get over the 'transition state / activated complex' (unstable state)

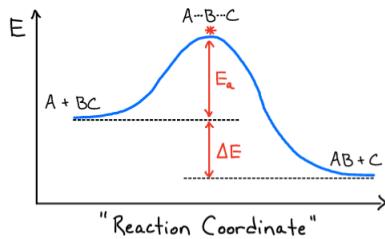


Figure 22: activation energy

- Molecules carry Energy into rxn via motion
- To react, $E_{\text{molecules}} > E_a$ → E_a large means few molecules can react
- larger E_a → slower rates
- ΔE has no relevance in rxn but it has in reverse rxn

12.2 Temperature ↔ Rate Law

- Rate: $k(T) = \left(\frac{\text{collisions}}{\text{time}} \right) \cdot \left(\frac{\text{collisions properly oriented}}{\text{collisions}} \right) \cdot \left(\frac{\text{molecules with } E > E_a}{\text{all molecules}} \right)$
- $k(T) = A \cdot e^{-\frac{E_a}{RT}}$
- Arrhenius Equation (ln on both sides): $\ln(k) = -\frac{E_a}{RT} + \ln(A)$
- for Temperature increases: $\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \cdot \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$

12.3 Reaction Mechanism

- write rxn as elementary rxn (only one bond breaks / forms, ex in Lecture 11)
- molecularity of rxn: number of molecules participating (see table below)

Molecularity	Elementary rxn	Rate law
Unimolecular	$A \rightarrow P$	$k[A]$
Bimolecular	$A + A \rightarrow P$	$k[A]^2$
Bimolecular	$A + B \rightarrow P$	$k[A][B]$
Termolecular	$A + A + A \rightarrow P$	$k[A]^3$
Termolecular	$A + A + B \rightarrow P$	$k[A]^2[B]$
Termolecular	$A + B + C \rightarrow P$	$k[A][B][C]$

the more molecules have to collide, the less likely the process is to happen

Rate laws for Elementary Reactions: $\alpha A + \beta B \rightarrow \gamma C + \delta D = k[A]^m[B]^n$ for elementary rxns: $m = \alpha$ and $n = \beta$ but not the other way around

determine rxn mechanism measure rates → propose mechanism → Check consistency

12.4 Catalysts

Increase rxn rate but not produced / consumed in overall rxn

- increase A: better orient molecules for rxn
- lower E_a : lower energy of transition state / new mechanism
- can lead to multistep rxn (multiple peaks in Energy plot)
- Homogeneous (reactants, products and catalysts are in the same phase)
- Heterogeneous (-"- in different phases)
- Natural Catalysts: Enzymes

13 Chemical Equilibrium

Dynamic Equilibrium = 2 processes balance (steady state), that means $A \rightleftharpoons B$

Chemical equilibrium occurs when forward and reverse rate are equal (for elementary rxns): $k_f[A] = k_r[B] \rightarrow \frac{[B]}{[A]} = \frac{k_f}{k_r} = \text{equilibrium konst}$

- closed system
- concentrations do not change anymore when they have reached an equilibrium
- rxns still occur
- system always moves to equilibrium concentrations

13.1 Mass Action

K_c = equilibrium constant for molarity concentrations **at equilibrium** for $\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$: $K_c = \frac{[C]^\gamma \cdot [D]^\delta}{[A]^\alpha \cdot [B]^\beta}$ For pressure: $K_p = \frac{[P_C]^\gamma \cdot [P_D]^\delta}{[P_A]^\alpha \cdot [P_B]^\beta} = K_c(R \cdot T)^{\Delta n} = K_c(R \cdot T)^{(\gamma+\delta)-(\alpha+\beta)}$ (see ideal gas law)

- all rxns behave like elementary rxns near equilibrium → Equilibrium constant unitless
- related to activities (comparing actual to reference concentration or pressure)

- $a_i = \frac{[i]}{1M} = \frac{P_i}{1bar}$ unitless
- $K = \frac{[a_C]^\gamma \cdot [a_D]^\delta}{[a_A]^\alpha \cdot [a_B]^\beta}$ is therefore also unitless
- $K \gg 1$: Equilibrium to right, products dominate, inverse for $K \ll 1$

13.2 Reaction Quotient

before equilibrium: $Q = \frac{[C]^\gamma \cdot [D]^\delta}{[A]^\alpha \cdot [B]^\beta}$

- $Q < C$: forward rxn dominates, inverse for $Q > C$

13.3 generally

- K for reverse reaction is $\frac{1}{K}$
- rxn multiplied with λ : $K' = (K)^\lambda$
- multistep rxn: $K = K_1 \cdot K_2$
- write rxn with K as same rxn written differently leads to different K
- Homogeneous equilibria: same phase
- Heterogeneous equilibria: different phase (exclude remaining pure substances from K as pure substances have activities of 1)
- saturated solutions low solubility ionic solids: $K_c = K_{sp}$ (solubility product)

13.4 Le Chatelier's Principle

If system at equilibrium is disturbed by change in T, P, [] –> system shifts its equilibrium to counteract disturbance

- Concentration change: use formula for Q
- Temperature change: treat heat like added reactant due to interaction of heat and rate law
 - Endothermic: $A + \Delta \rightleftharpoons B$
 - Exothermic: $A \rightleftharpoons B + \Delta$
- pressure changes: higher pressure –> shifts to side with fewer moles, inverse for lower pressure
- Catalysts do not change K, but equilibrium is reached faster

13.5 relation to thermodynamics

- $Q = K - > \Delta G = 0$ as rxn is neither spontaneous, nor non-spontaneous
- $\Delta G = 0 = \Delta G^\circ + RT \cdot \ln(K) - > \Delta G^\circ = -RT \cdot \ln(K) - > K = e^{-\frac{\Delta G^\circ}{RT}}$

14 Acids and Bases

only for aqueous solutions:

- Acid: transfer $[H^+]$ to $H_2O \rightarrow$ increases $[H^+] / [H_3O^+]$
- Base: accept H^+ from H_2O increases $[OH^-]$
- $H^+ + H_2O \rightarrow H_3O^+$ is really what happens
- proton transfer itself is applicable beyond water (Bronsted-Lowry)
- Autoionization of water: $H_2O(l) + H_2O(l) \rightleftharpoons OH^-(aq) + H_3O^+(aq)$
- $K_C = [OH^-][H_3O^+] = K_w = 10^{-14}(25^\circ C)$, in every aqueous solution
- If $[H_3O^+] > [OH^-] \rightarrow$ "acidic" ($pH < 7$), else "basic" ($pH > 7$)

14.1 p-Scales

indicates order of magnitude of $[H_3O^+]$ $pH = -\log[H_3O^+]$ with 14 magnitudes because $K_w = [OH^-][H_3O^+] = 10^{-14}$

$$pOH = -\log[OH^-] \quad pK_w = -\log(K_w) = -\log([H_3O^+][OH^-]) = pH + pOH = 14.00$$

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} \rightarrow pK_a = -\log[K_a]$$

$$K_b = \frac{[HB^+][OH^-]}{[B]} \rightarrow pK_b = -\log[K_b]$$

- when $pH = pK_a$: Acid is half ionized (einsetzen als Beweis)
- when $pH < pK_a$ acid exists as HA
- when $pH > pK_a$ acid exists as A^-

14.2 Acid-Base Pairs

- Amphiprotic substance can act as both acid or base (ex water)
- acid-dissociation constant

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$
 for $\underbrace{HA(aq)}_{\text{acid}} + \underbrace{H_2O(l)}_{\text{base}} \rightleftharpoons \underbrace{A^-(aq)}_{\text{conjugate base}} + \underbrace{H_3O^+(aq)}_{\text{conjugate acid}}$
- each acid HA / base B has conjugate base A^- / acid HB^+

14.3 Strength

similar for acids and bases

- strong acid: gives up all H^+ , conjugate non-basic
- weak acid: gives up some H^+ , conjugate weak base
- non-acidic: gives up no H^+ , conjugate strong base

14.4 Common-Ion Effect / Buffers

Substance with common ion is added to manipulate acid-base equilibria, ex strong electrolyte would completely dissociate

- Buffers protect against pH disturbances
- How: weak acid-base conjugate pair
 - $HA + OH^- \rightleftharpoons A^- + H_2O$
 - $H^- + H_3O^+ \rightleftharpoons HA + H_2O$
 - $\text{rightarrow} [H_3O^+] = K_a \frac{[HA]}{[A^-]}$
- possible to influence buffer pH using common-ion effect
- buffer $pH = pK_a + \log \left(\frac{[\text{base}]}{[\text{acid}]} \right)$
- effectively resist pH changes: $[HA] = [A^-]$ (buffer can be overwhelmed)

15 Redox (Also see section 4.4)

Electrochemistry: relationship between electricity and chemical rxns (Batteries)
Method to describe (acidic soln, example in lecture 14):

1. Divide into oxidation- and reduction half-rxn
2. Balance each half rxn (Balance all elements except H and O , Balance O by adding H_2O , balance H by adding H^+ , balance charge by adding e^-)
3. Multiply half rxns by integers to equate electrons
4. Add half rxns together
5. Check balance

basic soln (example in lecture 14):

1. Divide into oxidation- and reduction half-rxn (as above)
2. Add one OH^- to every H^+ on each side (to neutralize H^+ with OH^- , form H_2O , cancel H_2O on both sides)
3. last 3 steps as above

15.1 Batteries

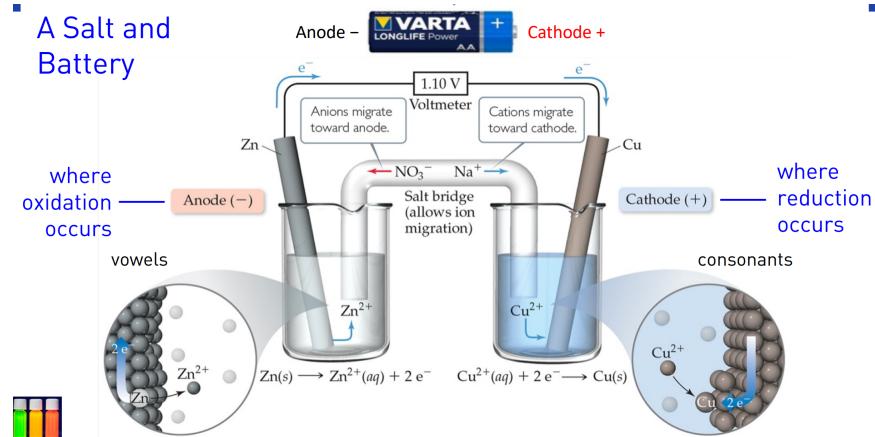


Figure 23: Battery

Components

- Electrodes (solid metals connected to circuit)
- Electrolyte (Liquid that moves ions, conducts electrical current)
- Salt bridge (Tube containing electrolyte (soln) so that Anions can move to anode, cations to cathode)

$$\text{Electrons flow from anode - to cathode + } 1V = \frac{1.6 \times 10^{-19} \text{ Joules}}{1.6 \times 10^{-19} \text{ Coulomb}}$$

15.2 Cell Potentials

- E°_{cell} = cell voltage at standard conditions
- Standard reduction potential E°_{red} = Potential energy available if reduced
- cell potential: $E^\circ_{\text{cell}} = E^\circ_{\text{red}}(\text{cathode}) - E^\circ_{\text{red}}(\text{anode})$

15.3 Standard Hydrogen Electrode (SHE)

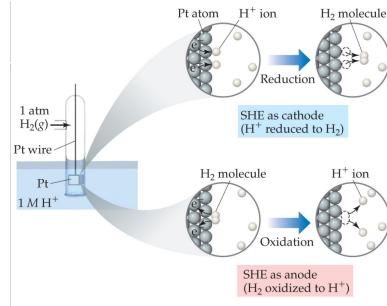


Figure 24: Standard hydrogen electrode (SHE)

- standard conditions
- can operate as anode or cathode
- to be useful $E^\circ_{\text{cell}} > 0$ (spontaneous flow of e^-)
- E°_{cell} does not depend on size
- full cell needed to determine potential
- E°_{red} can be determined by measuring with SHE
- greater E°_{red} means greater tendency for reduction

15.4 Gibbs Free Energy Connection

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

If $E^\circ_{\text{cell}} > 0$, $\Delta G^\circ < 0$ means spontaneous

16 Lists to learn

Charge	Formula	Name	Formula	Name
1+	H ⁺	hydrogen ion	NH ₄ ⁺	ammonium ion
	Li ⁺	lithium ion	Cu ⁺	copper(I) or cuprous ion
	Na ⁺	sodium ion		
	K ⁺	potassium ion		
	Cs ⁺	cesium ion		
	Ag ⁺	silver ion		
2+	Mg ²⁺	magnesium ion	Co ²⁺	cobalt(II) or cobaltous ion
	Ca ²⁺	calcium ion	Cu ²⁺	copper(II) or cupric ion
	Sr ²⁺	strontium ion	Fe ²⁺	iron(II) or ferrous ion
	Ba ²⁺	barium ion	Mn ²⁺	manganese(II) or manganous ion
	Zn ²⁺	zinc ion	Hg ₂ ²⁺	mercury(I) or mercurous ion
	Cd ²⁺	cadmium ion	Hg ²⁺	mercury(II) or mercuric ion
			Ni ²⁺	nickel(II) or nickelous ion
			Pb ²⁺	lead(II) or plumbous ion
			Sn ²⁺	tin(II) or stannous ion
3+	Al ³⁺	aluminum ion	Cr ³⁺	chromium(III) or chromic ion
			Fe ³⁺	iron(III) or ferric ion

Figure 25: common cations

Charge	Formula	Name	Formula	Name
1-	H ⁻	hydride ion	CH ₃ COO ⁻ (or C ₂ H ₃ O ₂ ⁻)	acetate ion
	F ⁻	fluoride ion	ClO ₃ ⁻	chlorate ion
	Cl ⁻	chloride ion	ClO ₄ ⁻	perchlorate ion
	Br ⁻	bromide ion	NO ₃ ⁻	nitrate ion
	I ⁻	iodide ion	MnO ₄ ⁻	permanganate ion
	CN ⁻	cyanide ion		
	OH ⁻	hydroxide ion		
2-	O ²⁻	oxide ion	CO ₃ ²⁻	carbonate ion
	O ₂ ²⁻	peroxide ion	CrO ₄ ²⁻	chromate ion
	S ²⁻	sulfide ion	Cr ₂ O ₇ ²⁻	dichromate ion
			SO ₄ ²⁻	sulfate ion
3-	N ³⁻	nitride ion	PO ₄ ³⁻	phosphate ion

Figure 26: common anions

Formula	Name	Characteristics
HCN	Hydrogen cyanide	Very toxic, slight odor of bitter almonds
H ₂ S	Hydrogen sulfide	Very toxic, odor of rotten eggs
CO	Carbon monoxide	Toxic, colorless, odorless
CO ₂	Carbon dioxide	Colorless, odorless
CH ₄	Methane	Colorless, odorless, flammable
C ₂ H ₄	Ethene (Ethylene)	Colorless, ripens fruit
C ₃ H ₈	Propane	Colorless, odorless, bottled gas
N ₂ O	Nitrous oxide	Colorless, sweet odor, laughing gas
NO ₂	Nitrogen dioxide	Toxic, red-brown, irritating odor
NH ₃	Ammonia	Colorless, pungent odor
SO ₂	Sulfur dioxide	Colorless, irritating odor

Figure 27: common gases

Soluble Ionic Compounds	Important Exceptions	
Compounds containing	NO_3^-	None
	CH_3COO^-	None
	Cl^-	Compounds of Ag^+ , Hg_2^{2+} , and Pb^{2+}
	Br^-	Compounds of Ag^+ , Hg_2^{2+} , and Pb^{2+}
	I^-	Compounds of Ag^+ , Hg_2^{2+} , and Pb^{2+}
	SO_4^{2-}	Compounds of Sr^{2+} , Ba^{2+} , Hg_2^{2+} , and Pb^{2+}
Insoluble Ionic Compounds	Important Exceptions	
Compounds containing	S^{2-}	Compounds of NH_4^+ , the alkali metal cations, Ca^{2+} , Sr^{2+} , and Ba^{2+}
	CO_3^{2-}	Compounds of NH_4^+ and the alkali metal cations
	PO_4^{3-}	Compounds of NH_4^+ and the alkali metal cations
	OH^-	Compounds of NH_4^+ , the alkali metal cations, Ca^{2+} , Sr^{2+} , and Ba^{2+}

Figure 28: Solubility of a few ionic compounds